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METHOD FOR THE MANUFACTURE OF ALUMINUM TRIHYDRATES
HAVING HIGH PORE VOLUMES, ALUMINUM TRIHYDRATES
MANUFACTURED ACCORDING TO THIS METHOD AND THEIR USE

- 5 The object of the invention is a method for the manufacture of aluminum trihydrate ($\text{Al}(\text{OH})_3$) by means of hydrolysis of aluminum alcoholates in aqueous, alkaline solution with addition of organic compounds, the so-manufactured aluminum trihydrates and their use as catalyst supports.
- 10 In general three aluminum trihydroxide modifications are known, in the following called "aluminum trihydrate": $\text{Al}(\text{OH})_3$, $\beta\text{-Al}(\text{OH})_3$ and $\gamma\text{-Al}(\text{OH})_3$.
- $\alpha\text{-Al}(\text{OH})_3$ (hydrargillite, gibbsite) is a natural product occurring as bauxite. It finds its principal industrial use as an input product of industrial purity in the winning of
- 15 aluminum (bauxite decomposition) and as an inexpensive starting material for manufacture of sodium aluminate.
- Due to its high level of impurities naturally occurring bauxite is not suitable as a catalyst support.
- 20 $\beta\text{-Al}(\text{OH})_3$ known as bayerite can be prepared by salt precipitation from aluminum sulfate and sodium aluminate solution or through hydrolysis of aluminum alcoholate. The latter variant is suitable, for preparing high purity bayerite while from the salt precipitation sodium and sulfate contaminated products precipitate. The high purity bayerite and its secondary product obtained by calcining find industrial application
- 25 in the manufacture of catalyst supports. Due to the crystalline nature (crystallite size of 30 to 40 nm measured at the 311-reflex) this material is not dispersable and consequently hard to process to paste-like masses for manufacture of extrudates, such as are employed in the manufacture of catalyst supports.
- 30 The manufacture of $\gamma\text{-Al}(\text{OH})_3$, also called nordstrandite, is likewise known. Due to the only small differences in the physical characteristics to bayerite, nordstrandite has no special technical significance. There is also the fact that the synthesis is not economical due to higher amounts of wash water is from a technical standpoint questionable environmentally and through the duration of the synthesis being more
- 35 than 3 days.

Aluminum hydroxides are manufactured by means of precipitation from aqueous solutions by utilization of a precipitation aid and other ways. Thus U.S. Patent 5,928,127 describes precipitation of an aluminum oxide sol from an aqueous solution by addition of sulfonic acids.

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From DE 195 22 946 furthermore a method is known for the manufacture of a finely divided aluminum hydroxide by reaction of aluminum alkoxides with other metal oxides at high shear stirring rates.

- 10 The known methods up to now for the manufacture of aluminum hydroxides have the disadvantage that the aluminum hydroxides obtained are not sufficiently pure for the manufacture of catalyst supports or are not available in a uniform modification.

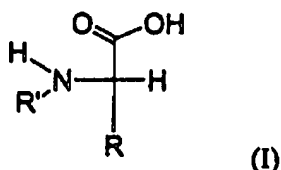
It is the problem of the present invention is to make available a method for
15 manufacture of aluminum trihydroxides (aluminum trihydrates) $\text{Al}(\text{OH})_3$, which have a high pore volume of greater than 0.6 ml/g, preferably greater than 0.8 ml/g (determined by N_2 adsorption), specially preferred of greater than 1.0 ml/g and smaller crystallite sizes and higher purity, e.g. less than 40 ppm sodium and smaller than 50 ppm sulfate, as well as aluminum trihydroxide, for use as a catalyst support.

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This problem is solved by means of a method in accordance with claim 1 or the other independent claims, preferred embodiments or the subject of the subclaims or described as follows.

- 25 The two parameters high pore volumes and small crystallite size are up to now not described for naturally occurring or industrially produced aluminum trihydrates. The avenue to these new kinds of compounds is of great significance for the further development of catalyst carriers.

- 30 The object of the invention is a method for the manufacture of high purity aluminum trihydrates $\text{Al}(\text{OH})_3$, by means of hydrolysis of aluminum alcoholates, wherein these have at least one alcohol group, preferably 3 alcohol groups, and the alcohol groups preferably have 1 to 24, specially preferred 4 to 8 carbon atoms, in aqueous alkaline solution with addition of organic compounds, which have at least one carboxyl
35 group and at least one amine group and preferably additionally at least one hydroxyl group. Preferably the organic compound is an amino acid of the general formula I or its salt:



with R equal to H or a hydrocarbon group having
1 to 20 carbon atoms and if necessary other
functional groups, e.g. one or two,
R' equal to H, or

carrying C₁ to C₅ alkyl, if necessary other functional
groups, e.g. one or two,

Preferably the R group of the amino acid has a hydroxyl group -OH. Specially
preferred as amino acids L-serin, aspartic acid, glycine or L-leucin are employed.

So far as the organic compounds employed in accordance with the invention are
present as salts, the ammonium salts, including for example the alkanolammonium
salts are preferred.

In accordance with the invention the organic compound is preferably present in
amounts from 0.1 to 1 wt%, specially preferred 0.2 to 0.3 wt% calculated as free
acid and in relation to the total mass of the aqueous hydrolysis employed in the
aqueous hydrolysis receiver.

The aluminum trihydrate manufactured according to the method in accordance with
the invention is preferably present as α -Al(OH)₃ or as γ -Al(OH)₃, that is it preferably
has a gibbsite or nordstrandite structure.

The hydrolysis is carried out in accordance with the invention at temperatures
between 0 °C and 60 °C and specially preferred at 30 °C to 40 °C. The aqueous,
alkaline solution thereby preferably has a pH value from 8 to 13, especially from 9
to 12.

The aluminum trihydrates manufactured according to the method in accordance with the invention preferably have a pore volume of 0.6 to 1.5 ml/g, preferably 0.8 to 1.1 ml/g.

- 5 The object of the invention is furthermore the use of the aluminum trihydrate manufactured according to the method in accordance with the invention preferably as a catalyst support.

- 10 The method in accordance with the invention makes possible the synthesis of new type nordstrandite and gibbsite similar trihydrates through hydrolysis of aluminum alcoholates in aqueous alkaline solution with addition of organic compounds which have at least one carboxyl and one amine group. Amino acids are specially suited.

- 15 By utilization of different amino acids the connections between the nature of the side group of the amino acid employed and the trihydrate obtained are reflected. In many syntheses a mixture of bayerite, gibbsite and nordstrandite is obtained, as a rule however according to the method in accordance with the invention gibbsite and/or nordstrandite are formed.

- 20 The presence of amino acid compounds leads to aluminum trihydrates with increased pore volumes. Amino acids like L-leucin, glycine, L-serin, L-threonine. L-aspartic acid, L-glutamic acid, L-cysteine, as well as their dimers cysteine and homocysteine lead to formation of nordstrandite and/or gibbsite-similar materials.

- 25 In the use of L-leucin (side groups $-\text{CH}_2\text{-CH}(\text{CH}_2)_2$) in the hydrolysis receiver a trihydrate with gibbsite structure precipitates. The same is true for L-cysteine, the dimer of cysteine and homocysteine in the hydrolysis receiver.

- 30 On the other hand glycine or amino acids with a hydroxide containing side group (L-serin: $\text{R} = -\text{CH}_2\text{-OH}$, aspartic acid: $\text{R} = -\text{CH}_2\text{-COOH}$) preferably lead to precipitation in the nordstrandite form. Glycine, L-serin, aspartic acid and L-threonin preferably lead to precipitation in the nordstrandite form.

- 35 An increase of the amount of amino acid in the hydrolysis receiver can hinder the trihydrate precipitation up to the complete suppression in favor of formation of an amorphous boehmite. A further lowering of the amount of amino acid favors the

precipitation of bayerite. In the use of e.g. glycine, 0.25 to 0.3 wt% is to be considered as the optimal amount in the receiver applied to the hydrolysis receiver, in order to obtain as pure a nordstrandite phase as possible.

- 5 It is furthermore the object of the invention, the aluminumtrihydrates to undergo an aging process in a further step after the hydrolysis. The aging is preferable carried out between 30 °C and 100 °C, especially between 40 °C and 60 °C, preferably for a period of time of more than 1 h, preferably more than 2 h. Independently hereof the solid material concentration of the slurry to be aged amounts preferably to 2 to 17
10 wt%, preferably 3 to 5 wt%, calculated as Al_2O_3 and in relation to the total weight of the slurry.

- The new type of trihydrate described in this method is distinguished by having a pore volume greater than 0.6, preferably greater than 0.8 ml/g. A high product purity
15 is achieved through the manufacture that is the hydrolysis of purified aluminum alcoholate. Through a smaller crystallite size than with conventional bayerite, the trihydrates are psrtially dispersable and consequently have very good processability to paste-like masses for manufacture by extrusion.

- 20 Alkaline solutions in the sense of the invention are aqueous solutions having a pH greater than 8, preferably 9-12. The alkaline pH value of the hydrolysis receiver can however be achieved by addition of suitable substances, such as e.g. ammonia, alkali solution or pH adjusting materials.

- 25 In accordance with the invention for the manufacture of aluminum trihydrates, aluminum alcoholates are employed. The aluminum alcoholate can for example be prepared by the Ziegler method, wherein preferably a purification takes place through filtration. As aluminum alcoholates C_1 to C_{24} alcohols or their mixtures can be employed.

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Examples:

Example 1a (Comparison example)

- 457 g of water and 23 g of a 25% ammonia solution were warmed to 30 °C in a 2 l
35 three-neck flask. Into this receiver 400 g of aluminum hexanolate were added

dropwise in under 1 hour, while stirring and holding the temperature constant. Two immiscible phases were formed, an upper alcohol phase and an alumina-water phase.

- 5 After decanting the alcohol phase the alumina-water phase after further addition of water was aged for 5 h at 30 °C with stirring. After removal of the alcohol dissolved in the water a pH value was determined between 9.5 and 10.5 was determined and the alumina slurry dried.

Example 1b (Comparison Example)

- 10 For the preparation of bayerite from a salt solution, 100 g of sodium aluminate solution and 200 g of water were warmed to 30 °C in a 1 l three neck flask. Into this receiver aluminum sulfate solution was added while stirring and holding the temperature constant until a pH value of 10 was achieved. This addition was carried out in less than 45 minutes. Thereupon it was heated to 70 °C while stirring and aged
- 15 while holding the temperature constant for 30 minutes. The filter cake resulting from filtration of the warm reaction mixture was washed with 1.5 l of water and dried.

Example 2

The following substances were reacted analogously to Example 1a.

- 20 464 g water
 22.2 g ammonia solution (25%)
 1.4 g glycine in the receiver
 400 g aluminum hexanolate

- 25 Thereby the additional amino acid were already present along with the water and the ammonia solution in the three-neck flask before beginning the reaction.

Example 3

- Test implementation and the materials and amounts employed correspond to
- 30 Example 2. In deviating the alumina slurring was undergone before the 16 h drying at 50 °C with stirring for further aging.

Example 4 (nordstrandite)

- Test implementation took place analogously to Example 1a with the following added
- 35 amounts:

 232 g water
 11.1 g ammonia solution (25%)

0.6 g L-aspartic acid in the receiver
200 g aluminum hexanolate

Example 5 (Comparison Example, not in accordance with
the invention)

Test implementation took place analogously to Example 1a with the following added amounts:

232 g water
11.1 g ammonia solution (25%)
1.2 g L-aspartic acid in the receiver
200 g aluminum hexanolate

The test 5 was carried out with a higher amount of L-aspartic acid. The product obtained showed a boehmite structure as a result of the X-Ray structure analysis.

Example 6 (nordstrandite)

Test implementation took place analogously to Example 1a with the following added amounts:

232 g water
11.1 g ammonia solution (25%)
1.2 g L-serin in the receiver
200 g aluminum hexanolate

Example 7 (gibbsite/bayerite)

Test implementation took place analogously to Example 1a with the following added amounts:

232 g water
11.1 g ammonia solution (25%)
1.2 g L-leucin in the receiver
200 g aluminum hexanolate

Example 8 (gibbsite/boehmite)

Test implementation took place analogously to example 1a with the following added amounts:

232 g water
11.1 g ammonia solution (25%)
0.6 g L-cysteine in the receiver

200 g aluminum hexanolate

Example 9 (bayerite)

Implementation took place analogously to Example 1a with the following added
5 amounts:

232 g water
11.1 g ammonia solution (25%)
0.6 g L-tyrosine in the receiver
10 200 g aluminumhexanolate

Example 10 (Comparison Example)

500 g of 20% ethylenediamine solution was warmed to 30 °C in a 1 l three-neck
flask. Into this receiver 12.5 g of aluminum was added in powder form in portions in
15 less than a half an hour with stirring. Thereupon it was heated to 50 °C and held 3
days at this temperature with light stirring. After addition of a further 50 g of
ethylenediamine it was lightly stirred for a further 4 days. The reaction mixture was
now filtered and the resulting filter cake after being washed with water and ethanol
was dried.

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The phase behavior was determined by means of STA. The Simultaneous Thermal
Analysis (STA) comprises the Differential Thermal Analysis (DSC) and the
Thermogravimetry (TG). The heat-up rate amounted to 10 K/min with air flushing.
The surface area of the aluminum oxide was determined by means of an N₂ sorption
25 technique according to BET (DIN 66131). The pore volume and the average pore
radius were determined by means of N₂ sorption according to BJH (DIN 66134).

In figure 1 the X-ray diffraction diagram (Drucker AXS, D5000, with scintillation
counter and CuK_α radiation, 2θ = 6 to 80°) and in figure 2 the DSC/TG from Example
30 2 is presented.

Table 1
Properties of the Products
of Examples 1 through 10

5	#	Phase 1t. XRD	Surface Area m ² /g	Pore Volumes* ml/g	Avge. Pore Radius* nm
10	1a	bayerite	277	0.39	3
	1b	bayerite	311	0.37	3
	2	nordstrandite + little bayerite	272	0.89	6
	3	nordstrandite + little bayerite	286	1.04	7
	4	nordstrandite + little bayerite	266	0.81	6
15	5	boehmite	293	0.51	3
	6	nordstrandite + little bayerite	267	0.76	6
	7	amorph. Gibbsite + little bayerite	269	0.70	5
	8	amorph. Gibbsite + little bayerite	303	0.63	4
	9	bayerite	264	0.71	2
20	10	nordstrandite (Hauschild)	214	0.25	2

* the activation temperature was 550 °C for 3 hours